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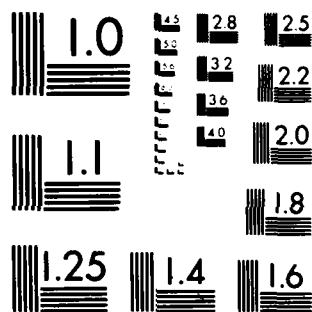
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MATTHEW J. KERPL
Chief, Technical

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Energetics and Collision
Dynamics of Electronic
Transition Lasers

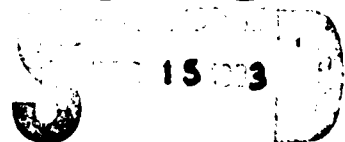


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Energetics and Collision
Dynamics of Electronic
Transition Lasers

Final Report

Contract No. F49620-81-C-0097

REPORTED BY

H. H. Michels
H. H. Michels

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the I_2 and I_3 molecules and the mechanisms of the I_2/O_2 1A_g dissociation kinetics. In addition, a study of the electronic structure of the NaMg system was carried out to evaluate its potential as a excimer laser.

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FOREWORD

This report was prepared for the Air Force Office of Scientific Research, United States Air Force by the United Technologies Research Center, East Hartford, Connecticut, under Contract F49620-81-C-0097, Project-Task No. 2303/B1. The performance period for the technical program was from 1 August 1981 through 31 July 1983. The project monitor was Major William G. Thorpe, USAF.

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R83-925832

Energetics and Collision Dynamics of
Electronic Transition Lasers

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ABSTRACT

Knowledge of the partition of energy between the products of a chemical reaction is fundamental to the understanding of the dynamics of collisional reactions. Atom-atom and atom-molecule reactions that yield vibrationally excited diatomic molecules are of particular scientific and military interest. An understanding of the dynamics of the simplest of these reactions is a prerequisite for understanding more complicated gas phase reactions. A knowledge of at least limited regions of potential energy surfaces is of importance in analyzing the vibrational and rotational relaxation rates and can be utilized in a predictive fashion. In the low energy regime there are little data available on collision processes and experimental measurements are difficult. Thus, a program to develop theoretical techniques and construct computer programs for calculating potential energy surfaces and kinetic cross sections for simple collision processes is appropriate. The potential energy surfaces include both atom-atom and atom-diatom systems with special emphasis on molecular reactions yielding electronically excited products which have potential as visible or UV chemical lasers. These systems include metal oxides and halides, metal excimers and the noble gas-halides. This research developed techniques and computational schemes for a priori prediction of the kinetics and the product distribution of atom-diatom reactions. This involved (1) improved calculation techniques for potential energy surfaces for the reactants and products, (2) quantum and classical mechanical calculations of the dynamics of the reaction and (3) detailed calculations for systems with high potential as electronic transition lasers.

Energetics and Collision Dynamics
of Electronic Transition Lasers

STATEMENT OF WORK

Perform a theoretical research investigation of the electronic structure and energetics of molecular systems and on chemical reactions in such systems which would yield a sufficient density of excited electronic species capable of lasing on an electronic transition. This investigation will include the calculation of electronic wavefunctions and energies as a function of internuclear separation followed by calculations of electronic transition moments for systems selected as typical of this class, and which appear to offer a high potential as candidate lasers. In addition, research shall be carried out related to the development of practical computational techniques for prediction of the kinetics and the product distribution of chemical reactions involving electronically excited reactants or products. Experimental data will be iteratively examined and integrated with the results generated from this theoretical investigation. The computations shall be carried out using density functional and ab initio methods, using computer codes developed or modified at this Center. Specifically, this investigation shall comprise the following:

a. Perform during the 1 August 1981 - 31 July 1982 performance period, quantum mechanical calculations of molecular electronic states of the following systems: I_2^* , MgO^* , Mg^*-Ca^* , and Mg^*-X where X represents a candidate laser species for excitation transfer from Mg^* .

b. Perform during the period 1 August 1982 - 31 July 1983, quantum mechanical calculations of the molecular states for the species listed in (a) above and carry out an analysis of the kinetic branching ratios and predicted product distributions of Mg^* and I_2/O_2 reactions.

REVIEW OF TECHNICAL EFFORT

Calculations of the dynamics of molecular collisions are ordinarily carried out with the aid of the Born-Oppenheimer separation of the electronic and nuclear motion. One proceeds by calculating the electronic energy as a function of the positions of the nuclei, which are assumed to be stationary. This electronic energy, plus the electrostatic repulsion between the nuclei, defines a potential energy hypersurface on which the nuclei may be regarded as moving. A potential energy hypersurface defined in this way is referred to as adiabatic, and is appropriate for describing the nuclear motion in the limit of low velocity. There are many collisions for which an adiabatic potential energy hypersurface provides an adequate description. However, most reactive collisions and many collisions which do not lead to reaction are inadequately described by an adiabatic potential energy hypersurface. These collisions are characterized by velocities of nuclear motion sufficient to affect adversely the Born-Oppenheimer separation, with the result that the overall wavefunction must be described as a superposition of terms involving different electronic energy states. Under these conditions, it will be useful to consider adiabatic potential energy hypersurfaces corresponding to all electronic states relevant to the overall wavefunction.

When the different potential energy hypersurfaces are well separated in energy, the nuclear motion can ordinarily be described in terms of motion on a single hypersurface. However, when two or more hypersurfaces are close in energy, they can be expected to mix appreciably in the overall wavefunction, and it will then be necessary not only to calculate the hypersurfaces but also to calculate the quantities needed to discuss their mixing in the overall wavefunction.

The calculation of a point on a potential energy hypersurface is equivalent to calculating the energy of a diatomic or polyatomic system for a specified nuclear configuration, and therefore will present considerable practical computational difficulty. For certain problems or nuclear configurations, the maximum possible accuracy will be needed and under these conditions relatively elaborate ab initio methods are indicated. Under other conditions, it may be possible to use less elaborate and more rapid computational methods, and density functional or other approaches may then prove useful.

A knowledge of at least limited regions of potential energy surfaces is of importance in analyzing the electronic, vibrational and rotational relaxation rates in chemical laser systems. These relative relaxation rates govern both the feasibility of lasing and the power that is potentially available. Such relaxation rates are governed by long-range forces between atomic and

molecular fragments and thus knowledge of the dissociation behavior represented by the potential energy surfaces for the laser system can be used in calculations of the kinetic behavior.

Our research effort has been devoted to the theoretical development of computational techniques for the prediction of potential energy surfaces, and to studies of the energetics of prototype electronic transition laser systems, the prediction of the radiative lifetimes of electronically excited species, and studies of photon energy loss paths such as photoabsorption or ionization of the upper excited electronic states. The goal of this research program was to develop a technical information base in support of the development of a practical chemical laser system operating on an electronic transition.

RESEARCH PROGRESS DURING THE CONTRACT PERIOD

For several years this Center has been involved in detailed ab initio quantum mechanical studies of the electronic structure, radiative, and kinetic properties of diatomic and polyatomic molecules. These studies have focused on air molecules and metal oxides, with applications to weapons technology, and on species which show promise as candidate laser molecules.

Our initial quantum mechanical studies dealt with the electronic structure and radiative lifetimes of the air system and certain diatomic metal oxide species which may be of abundance in the perturbed atmosphere following a thermonuclear explosion. Such diatomic species commonly exhibit strong LWIR radiation and a quantitative measure of this effect is needed to analyze the atmospheric kinetics. These studies were carried out using methods of molecular quantum mechanics coupled with available spectroscopic information on excited electronic states.

As an outgrowth of this research, a narrower study of certain classes of metal oxides and halides was initiated with the intent to screen such systems for candidates which might show potential as visible or UV electronic transition lasers. The criteria were to uncover systems having a low-lying excited state with a reasonably long radiative lifetime and situated energetically such that an inversion of population with respect to the dominant transitions to the ground state was possible. The systems under investigation to date include the group IIA metal oxides (BeO-BaO), the group IVB metal fluorides (SiF, GeF, SnF), the group IVB metal oxides (SiO-PbO), NF, MgF, AlF and the thirteen electron sequence: N_2^+ , CN, BO and BeF. These last systems have a common chemistry of their electronically excited states including a common $A^2\Pi \rightarrow X^2\Sigma^+$ Meinel transition, $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ first negative transition and a possible metastable $a^4\Sigma^+ \rightarrow X^2\Sigma^+$ transition.

As a result of these investigations, which were mainly carried out under Air Force sponsorship, this Center has available a large data base of calculated electronic energies and transition probabilities for metal oxide and halide systems. This base includes calculations for the ground and many electronically excited states of these molecules. Several of these systems have been analyzed in detail and their potential as candidates for electronic transition lasers has been evaluated (Refs. 1-5). These studies form a sound basis for analysis of such molecules as candidate laser systems. To the best of our knowledge, no other laboratory in the country has such an extensive catalogue of theoretical calculations of the electronic structure of metal oxides and halides or our computational experience with these types of molecules. In addition, UTRC has fully developed sophisticated computer programs for studying both diatomic and polyatomic molecules. These programs have been extensively used at UTRC and at the Air Force computational laboratories at AFWL, Kirtland Air Force Base and AFGL, Hanscom Field.

In addition to our studies of metal oxide and halide systems, a parallel theoretical research effort was directed toward analyzing the electronic structure of excimer laser systems. This program was concerned with a study of the energetics of the noble gas halides and noble gas dimer and trimer molecular ions and studies of candidate noble gas laser molecules operating on an electronic transition. The emphasis of the study of the noble gas halides was on the definition of potential energy curves, prediction of the radiative lifetimes of electronically excited states, and studies of photon energy loss paths such as photoabsorption and photoionization of the upper excited electronic states. A major effort of the study of the noble gas dimer and trimer ions was the definition of the potential energy curves and prediction of the photoabsorption cross-section for these species. Several of these systems have been evaluated in detail and the results have been reported in technical articles (Refs. 6-12).

As a continuation of our theoretical research of the energetics and collision dynamics of candidate laser systems, we have carried out an analysis of the energetics of Mg/MgO excitation transfer reactions, the spectroscopy of the low-lying states of the I_2 and I_3 molecules and the mechanisms of the I_2/O_2 $^1\Delta_g$ dissociation kinetics. These particular molecules were chosen because of their current AF interest as candidate laser systems or as species of importance in the kinetics of such systems. A review of our results of each system is given below.

I_2/I_3

Recent modeling analysis of I_2 dissociation suggests that the overall kinetic rate is approximately second order in $O_2[{}^1\Delta_g]$. One interpretation is that I_2 dissociation proceeds in two steps. The first involves $O_2[{}^1\Delta_g]$ excitation transfer to a reservoir state of the iodine system; the second, dissociation of this state to I atoms following collision of this reservoir state with a second $O_2[{}^1\Delta_g]$ molecule.

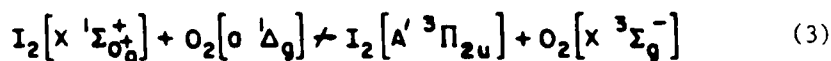
We have undertaken density functional studies of the electronic structure of I_2 and I_3 molecules in order to characterize the nature of the reservoir state in the I_2 dissociation mechanism. Detailed density functional studies of the I_2 molecule were carried out within a relativistic framework. The dissociation limits of these calculations were to the center-of-gravity of the $I[{}^2P] + I[{}^2P]$ asymptote. Spin-orbit coupling was handled using a perturbative approach in which only one-center contributions are added to the (A,S) coupled molecular states. We let

$$H(R) = H^{A,S}(R) + V^{SO} \quad (1)$$

where $\mathcal{H}^{\Lambda,S}(R)$ is the non-relativistic hamiltonian in (Λ, S) coupling and V^{SO} contains one-center contributions only and is not a function of the internuclear separation. The form of V^{SO} for $\Omega = 2u$ can be written as

$$V^{SO} = \begin{matrix} & \begin{matrix} {}^3\Pi_u & {}^3\Delta_u & {}^1\Delta_u & {}^3\Pi'_u \end{matrix} \\ \begin{matrix} {}^3\Pi_u \\ {}^3\Delta_u \\ {}^1\Delta_u \\ {}^3\Pi'_u \end{matrix} & \begin{vmatrix} -a & a & a & 0 \\ a & 0 & 0 & -a \\ a & 0 & 0 & a \\ 0 & -a & a & -a \end{vmatrix} \end{matrix} \quad (2)$$

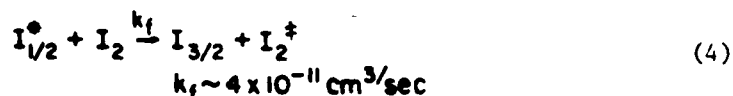
where $a = 1/2 \zeta_{sp} = 2534.38 \text{ cm}^{-1}$. This spin-orbit treatment accurately located both the $X^1\Sigma^+_{0g}$ and $B^3\Pi_{0u}$ states of I_2 but predicted the location of $A'^3\Pi_{1u}$ to be too low by $\sim 3000 \text{ cm}^{-1}$. The origin of the error lies in the assumption that only one-center contributions to V^{SO} are important. Apparently the ionic I^+I^- states are strongly mixed into parts of the low-lying valence state manifold for I_2 and our one-center treatment fails in these cases. Empirically adjusting our ${}^3\Pi_{2u}$ calculated curve by the known errors in the $A'^3\Pi_{1u}$ representation yields a prediction of $T_e = 9700 \text{ cm}^{-1}$ for the $A'^3\Pi_{2u}$ state. This is now in good agreement with the value reported by Tellinghuisen (Ref. 13). Our conclusion is that the $A'^3\Pi_{2u}$ state of I_2 is not accessible by the reaction



A composite of experimental and calculated potential curves for I_2 is given in Fig. 1 which indicates that there are no low-lying electronic states that are accessible to excitation via $O_2[a^1\Delta_g]$.

In Tables 1-3, we list several other dissociation pathways for I_2 . The $O_2^*[a^1\Delta_g]$ energy pooling mechanism suggested by Derwent and Thrush (Ref. 14) has been shown by Muller, et al. (Ref. 15) to be too slow to account for the dissociation of I_2 . Direct vibrational excitation of $I_2[X^1\Sigma^+_{0g}]$, followed by collision of I_2^* with a second $O_2[a^1\Delta_g]$ appears to be far too slow kinetically to be of importance. In Table 2, we indicate that an intermediate IO_2 species might be involved. Further work is in progress on this possibility. In Table 3, a vibrational pumping scheme for $O_2[a^1\Delta_g]$ is illustrated. An alternate scheme in which the electronic excitation of an $O_2[a^1\Delta_g]$ molecule is transferred to a vibrationally hot O_2 ground state molecule is apparently symmetry forbidden.

The possible role of I_3 in the dissociation of I_2 has apparently not been previously explored. Previous studies of trihalide molecules have been limited to matrix isolation studies of Cl_3 (Ref. 16) and Br_3 (Ref. 17). In Table 4, we show a correlation diagram for I_3 in both bent and linear conformations. Although there is no direct evidence for I_3 , it is known that I_2 is a very effective quencher of $I_{1/2}^*$ excitation via the reaction



Houston (Ref. 18) has recently made direct observations of Eq. (4) by pumping from several vibrationally excited states of I_2 to the $B^3\Pi_{0g}^+$ state and observing fluorescence back to the ground state. He finds population of I_2 (v'') up to $v'' = 40$, which is close to the thermodynamic limit. In Fig. 2, we illustrate our current analysis of the potential energy curves for I_3 . The $I_{1/2}^*$ deexcitation apparently goes by way of the $^2\Pi_{1/2u}$ ($^2A_1 + ^2B_2$) surface which is curve-crossed by the $^2\Sigma_{1/2u}^+$ (2A_1) surface arising from $I_{3/2} + I_2[X]$. The location of the curve-crossing indicates that ground state I_2 will be left with significant vibrational energy. Possible dissociation pathways which involve an intermediary I_3 species are illustrated in Table 5. Further computational studies of this system are now in progress.

Energetics of Mg/MgO Excitation Transfer Reactions

The chemical excitation of magnesium atoms to the lowest-lying metastable 3P state has been demonstrated (Ref. 19) through a consecutive reaction chain which involves:

- 1) the reaction of $N_2O[X^1\Sigma^+] + Mg [^1S]$ to form an intermediate complex, and
- 2) the decomposition of this complex by reaction with $CO[X^1\Sigma^+]$ to form $CO_2[X^1\Sigma_g^+] + Mg[^3P]$.

The overall utility of this reaction scheme depends on knowledge of the detailed kinetic mechanisms since the rate-determining step must be identified for analysis of the maximum conversion efficiency.

We have examined the potential energy surfaces for this reaction in order to shed light on the oxidation step kinetic mechanisms. The potential energy curves shown in Fig. 3 were constructed from available spectroscopic data for MgO (Refs. 20-22) and from ab initio molecular structure calculations

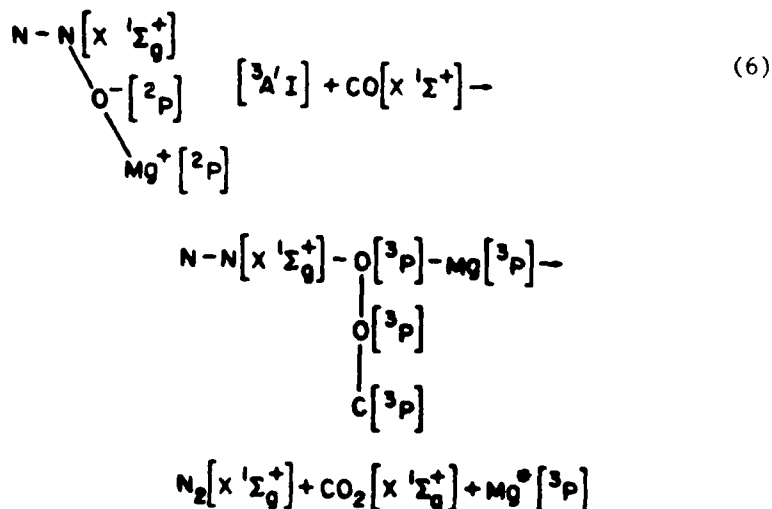
that were carried out at UTRC under AFOSR Contract F49620-81-C-0097. These potential curves for MgO illustrate a common behavior of the Group IIA metal oxides; all of the curves arising from $\text{Mg}[^1\text{S}]$ are repulsive in their long-range behavior owing to the closed-shell chemical nature of $\text{Mg}[^1\text{S}]$. The lowest lying reactive state of Mg is clearly the metastable $[^3\text{P}]$ state which diabatically correlates with $\text{O}[^3\text{P}]$ to form the ground $\text{X}^1\Sigma^+$ state and the low-lying $\text{a}^3\Pi$, $\text{A}^1\Pi$ and $\text{b}^3\Sigma^+$ electronically excited states of MgO.

These curves suggest that the initial reaction step is



This surface exhibits a long-range barrier of 0.27 eV (6.2 kcal/mol) at a Mg-O separation of 3.6 Å. In this region, this $^1\text{A}'$ surface is crossed by the ^1A charge transfer surface which correlates with the $\text{X}^1\Sigma^+$ and $\text{A}^1\Pi$ states of MgO. The structure of this charge transfer complex is that of an ionic Mg^+ ion attached to the bent N_2O^- molecular ion.

The $[^1\text{A}']$ charge transfer surface is very similar in nature to the lowest $[^3\text{A}']$ charge transfer surface (Ref. 23) and subcomponents in J-J coupling are common to both surfaces. It is therefore likely that these two charge transfer surfaces are mixed collisionally and are in pseudo-equilibrium. The $[^3\text{A}']$ surface of $\text{N}_2\text{-O-Mg}$ correlates to the $[\text{a}^3\Pi]$ and $[\text{b}^3\Sigma^+]$ states of MgO, which in turn correlate diabatically to the reaction of $\text{Mg}^*[^3\text{P}] + \text{O}[^3\text{P}]$. This can be represented schematically by



The rate determining step thus appears to be the initial formation of the N_2O -Mg complex owing to an indicated activation barrier of 6.2 kcal/mol. An apparent activation energy of 6.6 kcal/mol for this reaction has been reported by Kashirininov, et al. (Ref. 24), in good agreement with our calculated value. The appearance of continuum emission far down the reaction zone is further verification that this initial step is rate controlling in the overall oxidation kinetics. This barrier could be reduced experimentally either by thermal excitation of the $Mg[1S]$ atoms, by added vibration-rotation energy in N_2O or by an alternate choice for the oxidizer which may exhibit a smaller activation energy barrier. Further studies of the kinetic mechanisms for chemical production of $Mg^*[3P]$ are in progress. These include an examination of the importance of the energy pooling reaction

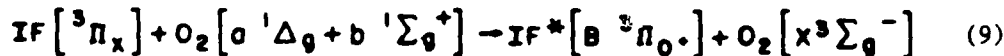
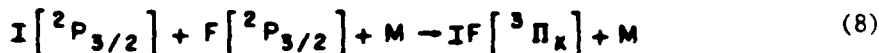


which has been reported (Ref. 25) to have a very large reaction rate of $\sim 9 \times 10^{-11} \text{ cm}^3/\text{sec}$.

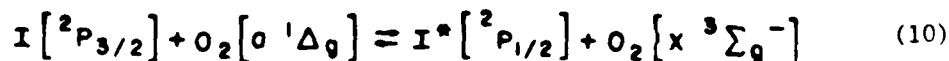
Energetics of IF Formation

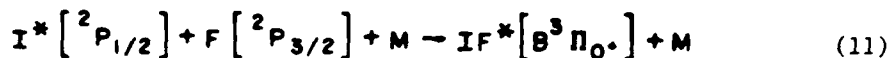
By optically pumping iodine monofluoride, IF, Davis and Hanco (Ref. 26) have demonstrated pulsed lasing on the $B^3\Pi_0^+ \rightarrow X^1\Sigma_0^+$ transition. Their studies have shown that lasing should occur on the $B(v'=0) \rightarrow X(v''=5)$ transition provided the vibrational levels $v'=0 \rightarrow 6$ are optically pumped. It is of interest to examine whether a chemical pumping scheme can be devised to populate the B state of IF within a kinetic time framework that would permit the IF ($B \rightarrow X$) system to lase.

Clyne, Coxon and Townsend (Ref. 27) have shown that a mixture of I, F and $O_2^*[a^1\Delta_g + b^1\Sigma_g^+]$ chemically produces the $B[3\Pi_0^+]$ state of IF. They proposed the mechanisms

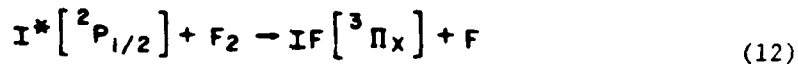


with $x = 2, 1$ or 0^- , or





These mechanisms have been studied more recently by Whitefield, Shea and Davis (Ref. 28), who added a third possibility

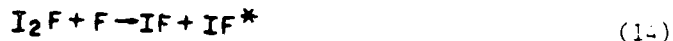


followed by reaction (9). The general validity of these pumping schemes hinges on knowledge of the energetics of the ${}^3\Pi_x$ manifold of states since this intermediate must be thermodynamically accessible.

An IF(B) formation mechanism that invokes the intermediate species I_2F has also been suggested (Refs. 29 and 30). An initial abstraction reaction:

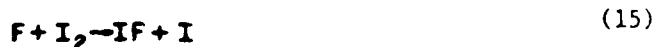


followed by:

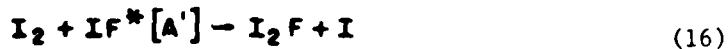


is apparently kinetically favored over the direct 4-center reaction (Refs. 31 and 32).

If the F_2 molecule is dissociated, an indirect mechanism for the formation of I_2F is given by the following reaction sequence.



This reaction is exothermic by ~ 30 kcal which may be sufficient to form IF in the $A'{}^3\Pi_2$ metastable state. The excitation energy of this state was uncertain, but assuming that A' is accessible, the reaction:



should be nearly resonant and may proceed at a rapid rate. Reaction (14) can then be invoked to form IF*.

Alternatively, I₂F could be made directly by the 3-body reaction

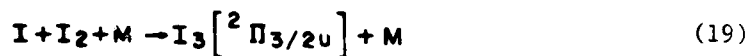


again followed by (14) to form IF. This reaction may not require a 3-body-adhesion to remove energy if the internal vibrational or electronic modes become excited, i.e.,

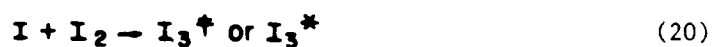


again followed by (14) to form IF*.

A similar trihalogen species to I₂F is I₃. It can be efficiently produced via the 3-body reaction:



or alternatively by:



Reaction (19) is also apparently energetic enough to form I₃ in the excited ²Σ_{1/2g} state. In either case, the reaction



is exothermic to form IF[X] and may be sufficiently energetic to form IF*[A'].

A correlation diagram for IF showing (Λ,S) → (J,J) coupling is given in Fig. 5. As indicated above, the exact location of the spin-orbit components of the low-lying ³Π state were uncertain but Whitefield, Shea and

Davis (Ref. 28) have suggested an excitation energy of 12,000 \rightarrow 15,000 for the lowest $A'^3\Pi_2$ state. This would appear to rule out reaction (16) as a possibility but additional evidence was needed.

Ab initio calculations of the low-lying electronic states of IF were carried out using our non-relativistic DIATOM code. Particular attention was directed to the low-lying $^1\Sigma$, $^3\Sigma$, $^1\Pi$, and $^3\Pi$ states of IF since our primary concern was the mixing of the various 0^+ component of these states and prediction of the location of the low-lying $A'^3\Pi_2$ and $A'^3\Pi_1$ states.

Since the spin-orbit effects in IF are inherently one-center on the I atom, a perturbative treatment of the calculated (Λ, S) coupled states was employed. The much smaller $F_{3/2} - F_{1/2}$ splitting was taken into account by simply scaling the calculated molecular curves to the correct F atom dissociation limits.

Our results for IF are given in Fig. 4 which illustrate a behavior very similar to that proposed by Clyne and McDermid (Ref. 33) for states of 0^+ symmetry. We find that the $B'^3\Pi_0^+$ state is predissociated by both the $c'^3\Pi_0^+$ and $Y'^3\Sigma_0^+$ states; the lowest predissociation is by $c'^3\Pi_0^+$ at the $v = 10$ level of the B state. Our calculated location for the $A'^3\Pi_2$ state is $T_{00} \sim 13,600 \text{ cm}^{-1}$, thus allowing reaction (12), at least for $^3\Pi_2$ symmetry of IF. Of particular interest is the lowest $^1\Pi_1$ state of IF which preliminary calculations indicate to be bound with $T_e \sim 18,000 \text{ cm}^{-1}$. This contrasts with the I_2 system where the lowest $^1\Pi_1$ state is found to be repulsive.

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this Contract have been prepared for publication in technical journals or presented at technical meetings. These papers and meetings are listed below. Abstracts of several of the published papers are included in the Appendices to this report.

A. Technical Reports in Journals and Books

1. "Laser Chemiluminescence of NaMg." D. J. Benard and H. H. Michels, Chemical Physics Letters, 86, 449, 1982
2. "Spherical Harmonic Expansion Techniques for Multi-Center Integrals Over STO's." H. H. Michels, ETO Multicenter Molecular Integrals, C. A. Weatherford and H. W. Jones (eds.), D. Reidel Pub. Co., pp. 103-121, 1982.
3. "Electronic Structure of I_2 and I_3 ." H. H. Michels and R. H. Hobbs, to be published in Chemical Physics Letters, 1983.
4. "Reaction of Ground and Excited State Yttrium Atoms with Oxygen," L. Lynds, B. A. Woody, H. H. Michels, and R. H. Hobbs, to be published in Chemical Physics Letters, 1983.
5. "Energetics and Mechanism of $Mg[P]$ Production in $Mg/N_2O/CO$ Flames." H. H. Michels and R. A. Meinzer, Chemical Physics Letters, 98, 6, 1983.
6. "Energetics of IF Formation." H. H. Michels, to be published in Chemical Physics Letters, 1983.

B. Technical Paper and Lecture Presentations

1. "Spherical Harmonic Expansion Techniques for Multicenter Integrals over STO's. A Reexamination for Vector Processing Computers." Presented at the Workshop on Multicenter Integrals, Tallahassee, Florida, 3-6 August 1981.
2. " I_2 Calculations." Presented at the Workshop on I_2/O_2 Dissociation Kinetics, Albuquerque, New Mexico, 10-11 September 1981.
3. "Theoretical Studies of the $O^+ + N_2$ Ion-Molecule Reaction." Presented at the 34th Gaseous Electronics Conference, Boston, Massachusetts, 20-23 October 1981.
4. Attended AFOSR Molecular Dynamics Contractors' Conference - AFWL, 9-12 November 1981.

5. "Electronic Structure of I_2 and I_3 ." Presented at the Tri-Service Chemical Laser Symposium, Albuquerque, New Mexico, 25-28 October 1982.
6. "Reaction of Ground and Excited State Yttrium Atoms with Oxygen," L. Lynds, B. A. Woody, H. H. Michels, and R. H. Hobbs. Presented at the 184th American Chemical Society National Meeting, Kansas City, Missouri, 12-17 September, 1982.
7. "Electronic Structure of I_2 and I_3 ," Presented at the AFOSR Contractors' Meeting, Colorado Springs, Colorado, 30 November - 3 December 1982.
8. "Spectroscopy of the I_3 Molecule," Presented at the 13th Winter Colloquium on Quantum Electronics, Snowbird, Utah, 12-14 January 1983.
9. "Theoretical Studies of the Electronic Structure of the I_2 and IF Molecules," Presented at the 13th Northeast Regional Meeting of the American Chemical Society, University of Hartford, West Hartford, Connecticut, 26-29 June 1983.
10. Attended AFOSR/AFGL Molecular Dynamics and Surface Chemistry Conference, AFGL, Hansom Air Force Base, Bedford, Massachusetts, 26-28 October 1983.

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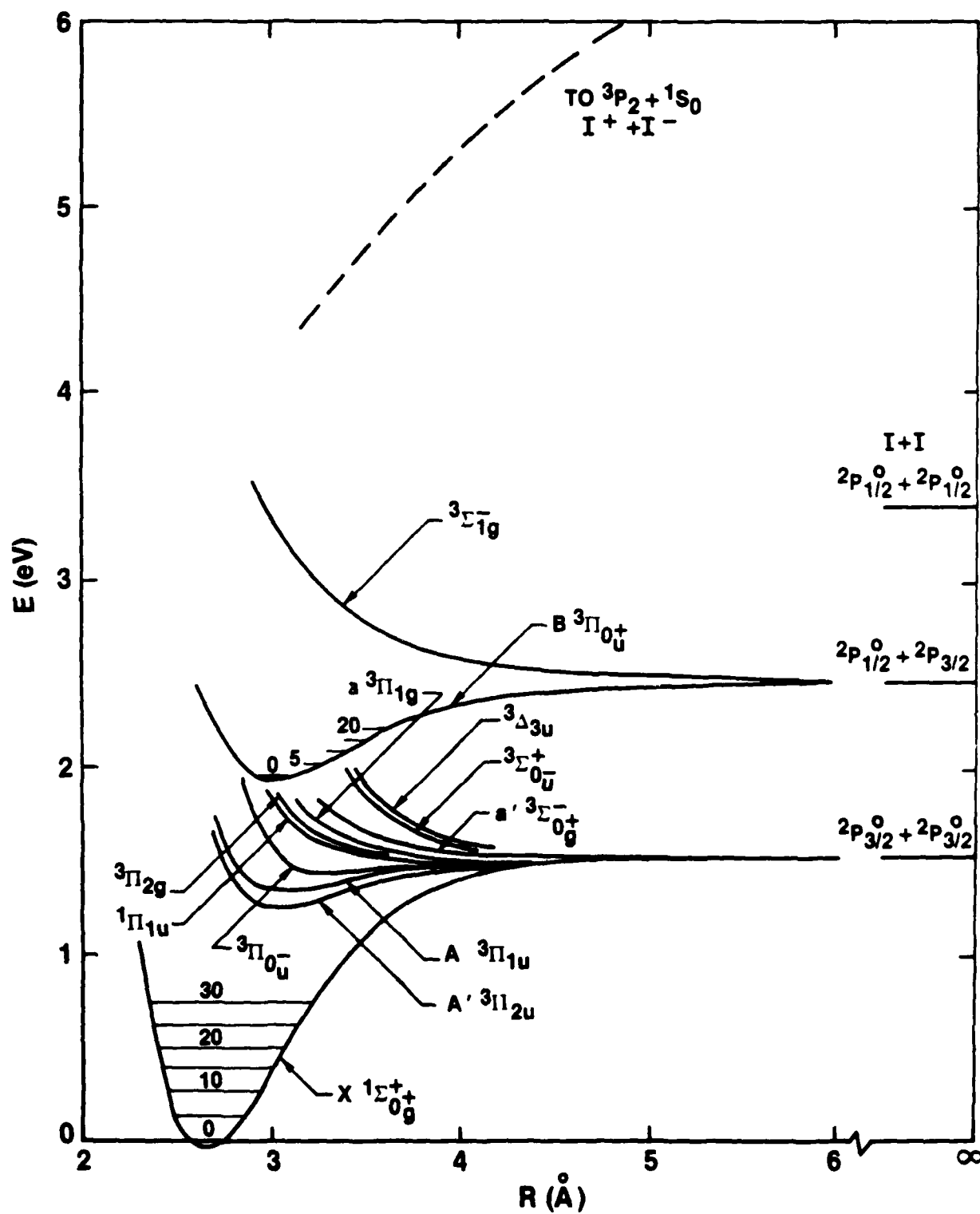
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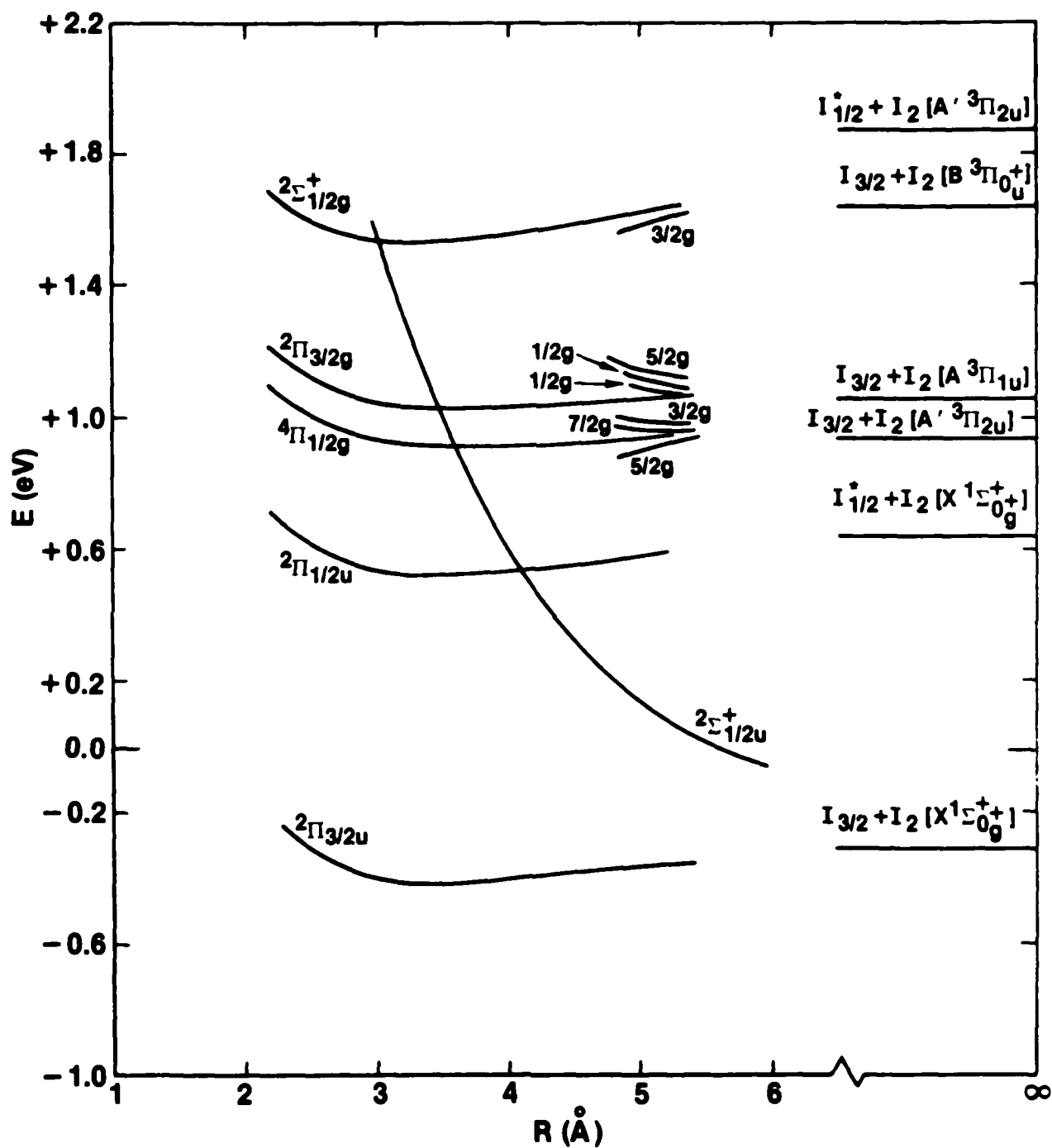
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POTENTIAL ENERGY CURVES FOR I₂

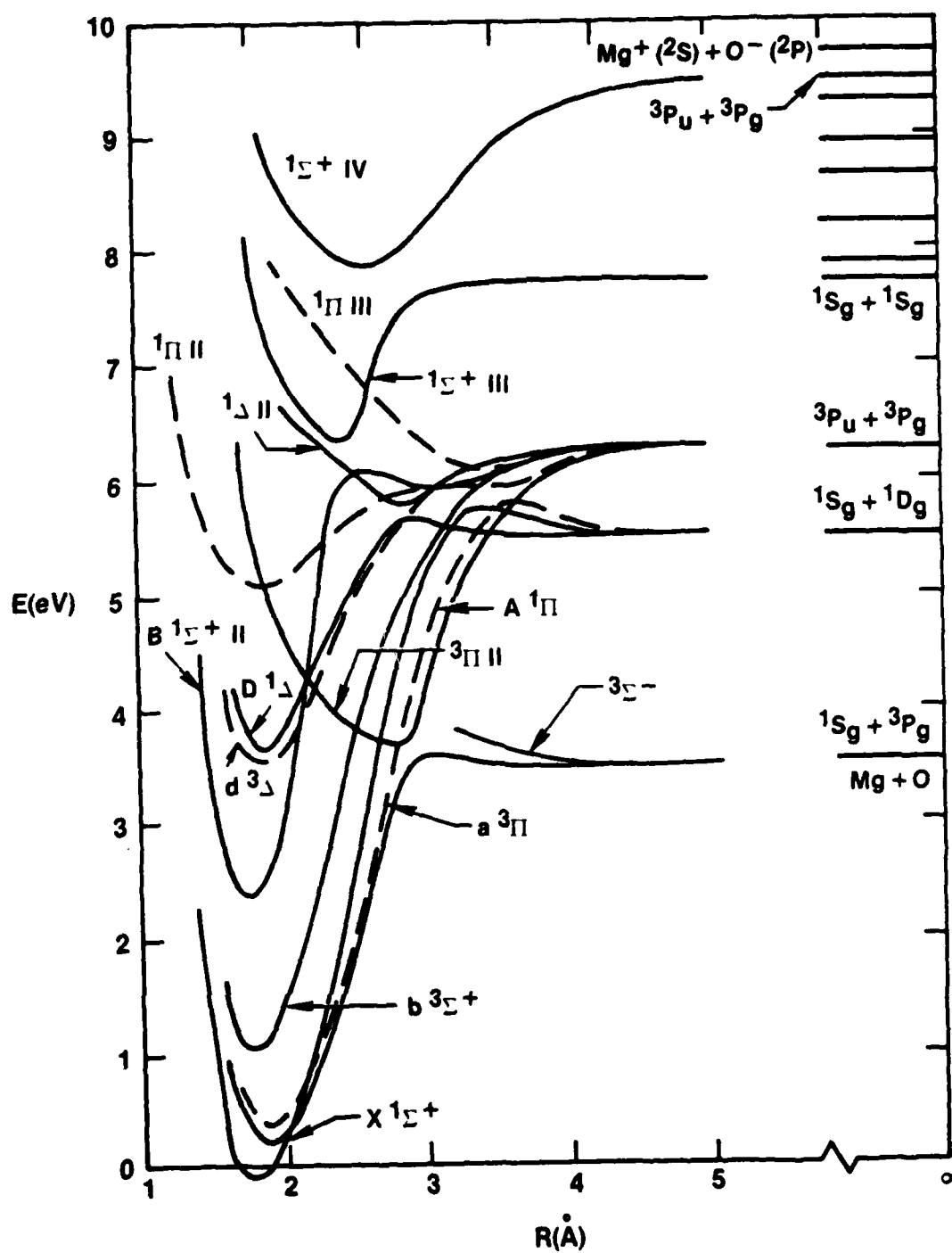


82-10-87-6

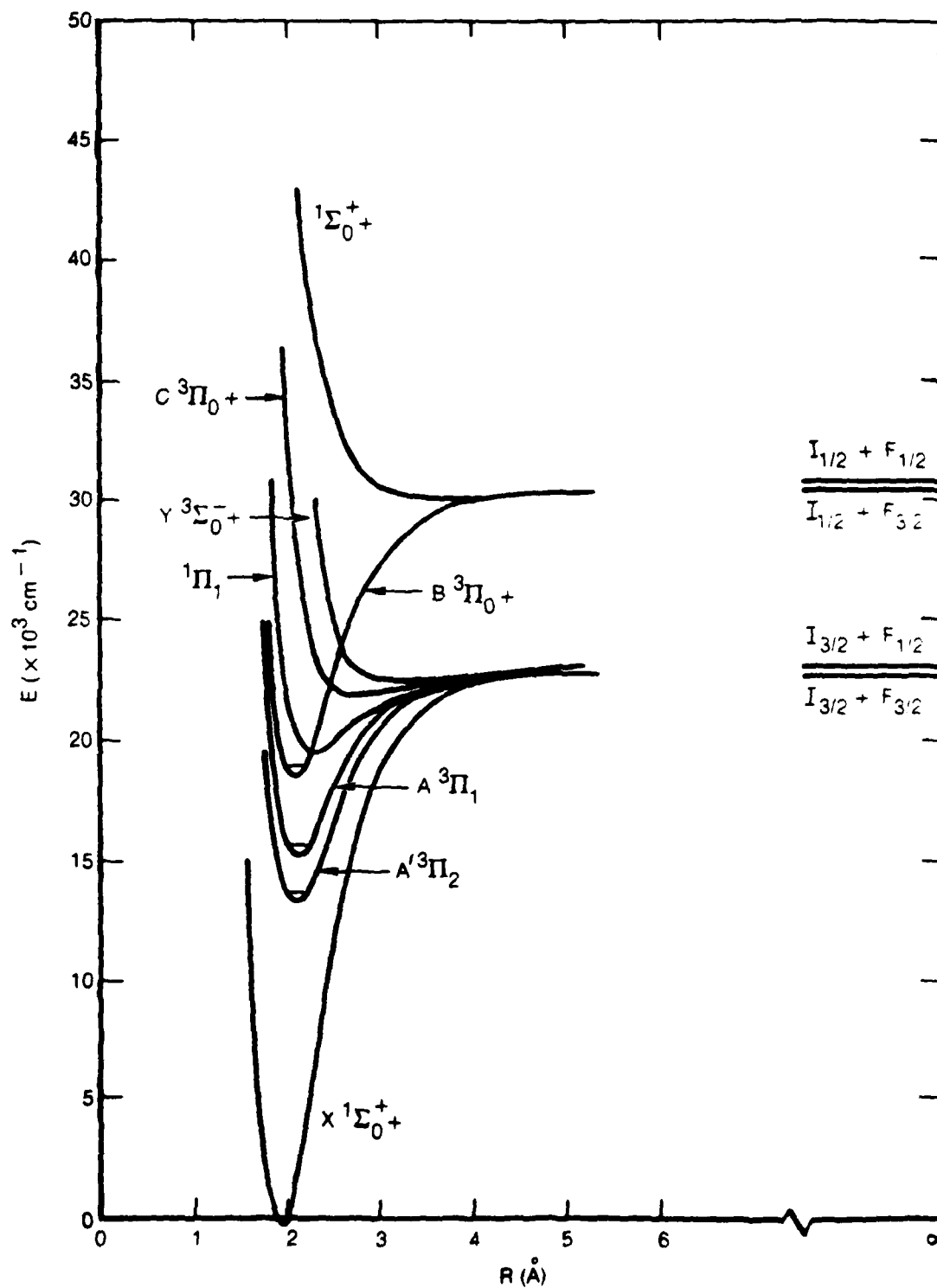
POTENTIAL ENERGY CURVES FOR I_3



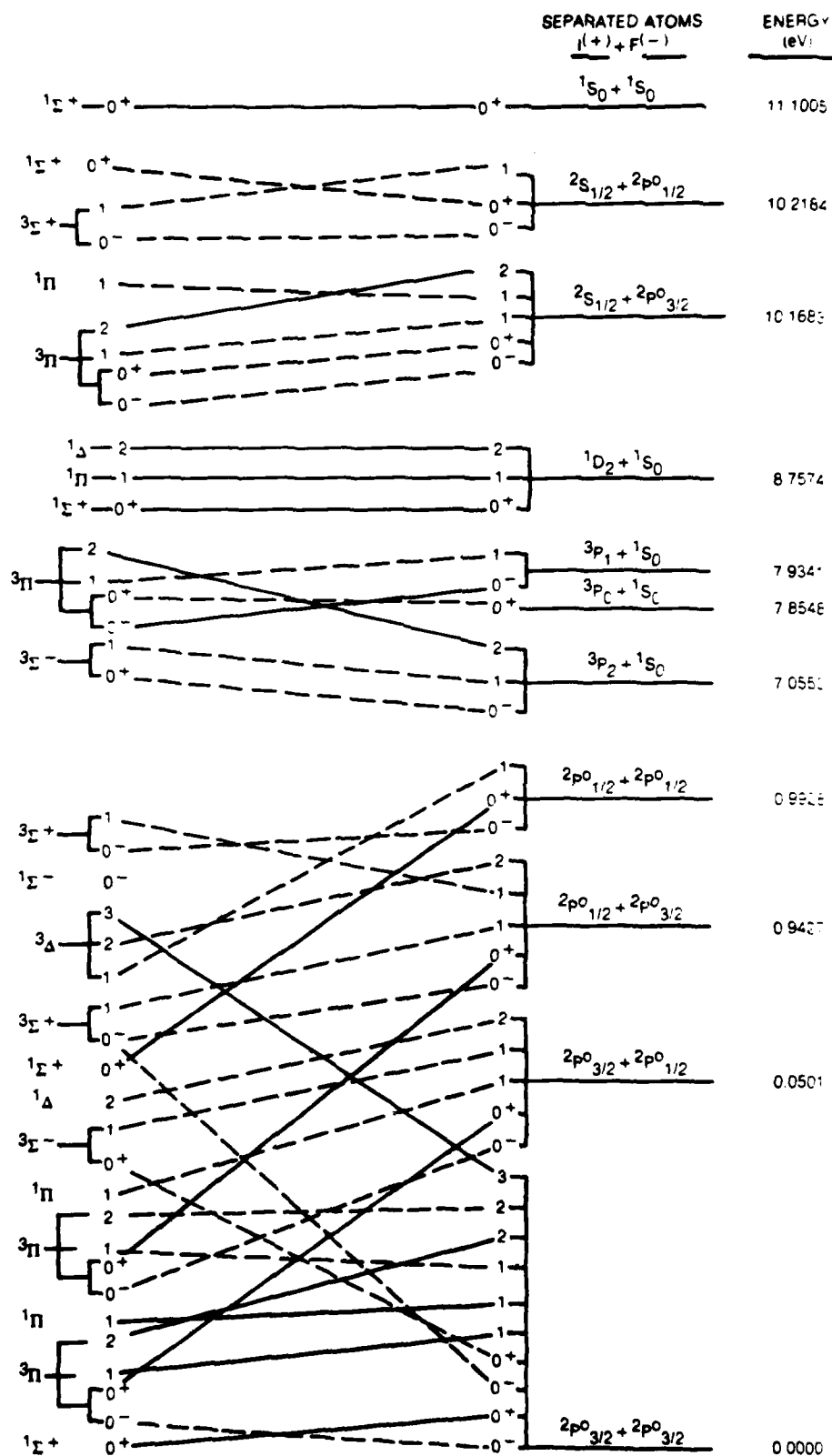
POTENTIAL ENERGY CURVES FOR MgO



DIABATIC ENERGY CURVES FOR IF



CORRELATION DIAGRAM FOR INTERMEDIATE COUPLING OF THE IF MOLECULE

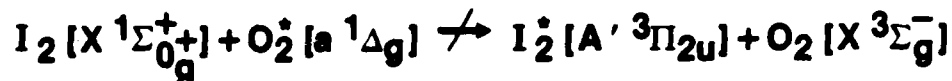
(UNIQUE ASSIGNMENTS FROM (J_1, J_2) TO (A-S) COUPLING ARE INDICATED BY SOLID LINES)

(A, S)

 (J_1, J_2)

REACTIONS FOR I₂ DISSOCIATION

DIRECT ELECTRONIC EXCITATION

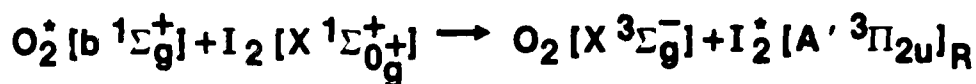


$\Delta E = +0.270 \text{ eV}$
ADIAB.

O₂^{*} [a ¹Δ_g] ENERGY POOLING



$\Delta E = -0.325 \text{ eV}$
SPIN FORBIDDEN



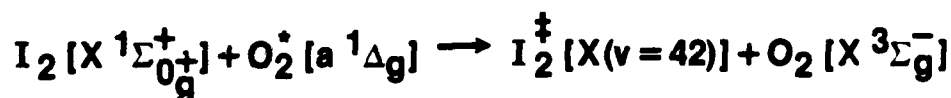
$\Delta E_{\text{VERT}} \approx \pm 0.05 \text{ eV}$



Slow overall rate (Heidner)

$$k \leq 8 \times 10^{-12} \text{ cm}^3/\text{sec}$$

DIRECT VIBRATIONAL EXCITATION



$\Delta E = -0.021 \text{ eV}$

Predicted Slow Rate:

$$k \leq 1 \times 10^{-14} \text{ cm}^3/\text{sec} \text{ (Gas Kinetic + FC)}$$

$$k \sim 0.7 \times 10^{-14} \text{ cm}^3/\text{sec} \text{ (Surprisal)}$$

TABLE 2

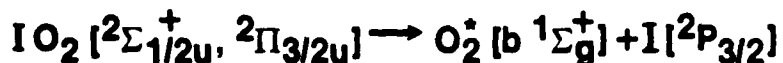
REACTIONS FOR I₂ DISSOCIATION

O₂^{*} [a ¹Δ_g] / I_{1/2}^{*} ENERGY POOLING

REACTANTS

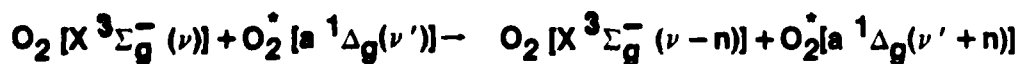


PRODUCTS



ALTHOUGH SPIN ALLOWED, THERE IS NO SIMPLE ADIABATIC SURFACE CONNECTING REACTANTS TO PRODUCTS. SECONDARY REACTIONS ARE THE SAME AS FOR O₂^{*} [a ¹Δ_g] ENERGY POOLING.

TABLE 3

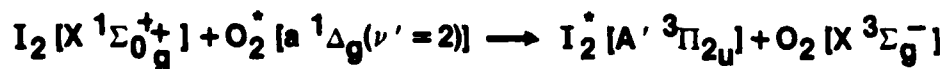
REACTIONS FOR I₂ DISSOCIATIONO₂^{*} [a ¹Δ_g] VIBRATIONAL PUMPING

$X^3\Sigma_g^-(\nu)$	$a^1\Delta_g(\nu')$		$X^3\Sigma_g^-(\nu-n)$	$a^1\Delta_g(\nu'+n)$	$\Delta E(\text{cm}^{-1})$
1	0	→	0	1	- 98.5
2	1	→	1	2	-100.4
1	1	→	0	2	-124.3

$$k \sim 3 \times 10^{-13} \text{ cm}^3/\text{sec} \text{ (Surprisal)}$$

2	0	→	0	2	-198.9
---	---	---	---	---	--------

$$k \sim 1 \times 10^{-13} \text{ cm}^3/\text{sec} \text{ (Surprisal)}$$



$$\Delta E = -0.09 \text{ eV}$$

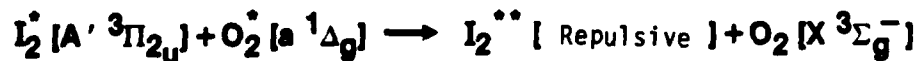


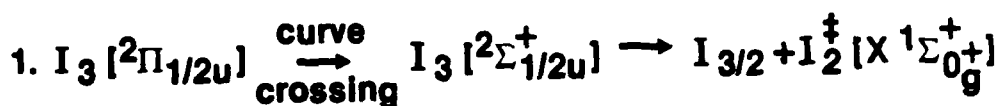
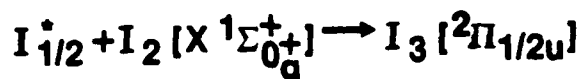
TABLE 4

I + I₂ CORRELATION DIAGRAM

<u>STATES OF ATOM + DIATOM</u>	<u>ENERGY (∞) (eV)</u>	<u>I₃ STATES</u>	
		<u>D_{∞h}</u>	<u>C_{2v}</u>
$2P_{3/2} + X \ 1\Sigma_{0g}^+$	0.0	$2\Sigma_{1/2u}^+, 2\Pi_{3/2u}$	$2A_1 (1/2), 2B_2 (3/2), 2A_1 (3/2)$
$2P_{1/2} + X \ 1\Sigma_{0g}^+$	0.943	$2\Pi_{1/2u}$	$2B_2 (1/2), 2A_1 (1/2)$
$2P_{3/2} + A' \ 3\Pi_{2u}$	1.246	$4\Delta_{7/2g}, 4\Pi_{5/2g}$ $4\Delta_{3/2g}, 4\Pi_{1/2g}$	$4A_1 (7/2), 4B_1 (7/2), 4A_2 (5/2), 4B_2 (5/2)$ $4A_1 (3/2), 4B_1 (3/2), 4A_2 (1/2), 4B_2 (1/2)$
$2P_{3/2} + A \ 3\Pi_{1u}$	1.361	$2\Delta_{5/2g}, 2\Pi_{3/2g}$ $4\Delta_{1/2g}, 4\Pi_{1/2g}$	$2A_1 (5/2), 2B_1 (5/2), 2A_2 (3/2), 2B_2 (3/2)$ $2A_1 (1/2), 2B_1 (1/2), 4A_2 (1/2), 4B_2 (1/2)$
$2P_{3/2} + B \ 3\Pi_{0u}^+$	1.944	$2\Sigma_{1/2g}^+, 4\Sigma_{3/2g}^+$	$2A_1 (1/2), 4A_1 (3/2)$
$2P_{1/2} + A' \ 3\Pi_{2u}$	2.188	$4\Delta_{5/2g}, 4\Pi_{3/2g}$	$4A_1 (5/2), 4B_1 (5/2), 4A_2 (3/2), 4B_2 (3/2)$
$2P_{3/2} + B' \ 3\Pi_{0u}$ (REP)	~ 2.2	$2\Sigma_{1/2g}^-, 4\Sigma_{3/2g}^-$	$2B_1 (1/2), 4B_1 (3/2)$
$2P_{1/2} + A \ 3\Pi_{1u}$	2.304	$2\Delta_{3/2g}, 2\Pi_{1/2g}$	$2A_1 (3/2), 2B_1 (3/2), 2A_2 (1/2), 2B_2 (1/2)$
$2P_{3/2} + B' \ 1\Pi_{1u}$ (REP)	~ 2.5	$2\Delta_{5/2g}, 2\Pi_{3/2g}$ $2\Sigma_{1/2g}^+, 2\Sigma_{1/2g}^-$	$2A_1 (5/2), 2B_1 (5/2), 2A_2 (3/2), 2B_2 (3/2)$ $2A_1 (1/2), 2B_1 (1/2)$

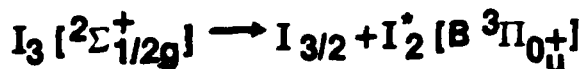
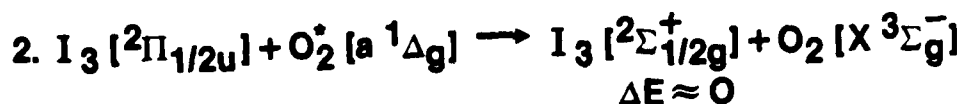
TABLE 5

POSSIBLE I₃ DISSOCIATION PATHWAYS

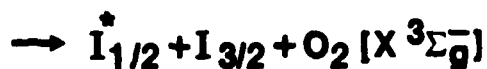
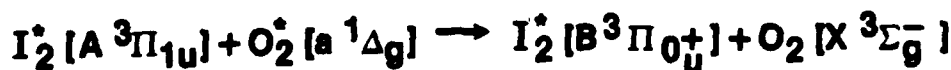
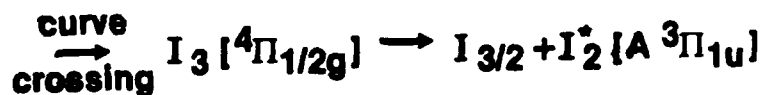
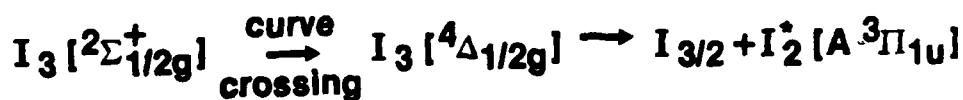


Paul Houston (Cornell) sees population

up to $\nu'' = 40$



$\Delta E = +0.11 \text{ eV}$



APPENDIX A

LASER INDUCED CHEMILUMINESCENCE OF NaMg^{*}

D. J. Benard
Kirtland Air Force Base
New Mexico 87117

†
H. H. Michels
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

An unstructured continuum emission centered at 670 nm was observed when Mg was added to an optically pumped heat pipe containing Na and K vapors, in good agreement with ab initio calculations of the NaMg potential energy curves. The corresponding excitation spectrum showed that the incident radiation was absorbed by NaK molecules on the X → C transitions.

*Published in Chemical Physics Letters, Vol. 86, 449-452, 1982.

†Supported in part by the Air Force Office of Scientific Research under Contract F49620-80-C-0095 and Contract F49620-81-C-0097.

APPENDIX B

SPHERICAL-HARMONIC EXPANSION TECHNIQUES FOR
MULTICENTER INTEGRALS OVER STO'S.

A REEXAMINATION FOR VECTOR PROCESSING COMPUTERS.*

H. H. Michels
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

In multicenter integral calculations, it is useful to express an atomic orbital as a spherical-harmonic expansion about a point displaced from the orbital's center. Through judicious choice of these expansion points, it is possible to calculate the general electron-repulsion integral for orbitals displaced at most by distances of the order of the bond lengths.

We have reexamined the utility of these orbital expansions for STO's in light of the availability of new computers with vector processing hardware. In particular, we have carried out studies for STO's typical of atoms through Ne. Impressive times have been achieved by new programs implemented on the CRAY-1 computer where the products of orbital λ -expansions are essentially reduced to several multiplication cycle times. Convergence problems still remain for core-like STO's (large λ 's) which suggests that a different approach should be implemented to handle this class of integrals.

*Published in Proceedings of the International Conference on ETO Multicenter Molecular Integrals, ed. C. A. Weatherford, D. Reidel Publishing Co., Netherlands, 1982. Supported in part by the Air Force Office of Scientific Research under Contract F49620-81-C-0097.

APPENDIC C

ELECTRONIC STRUCTURE OF I_2 and I_3^*

H. H. Michels and R. H. Hobbs
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

Density functional studies of the electronic structure of I_2 and I_3 molecules have been undertaken in order to characterize the nature of the reservoir state in the I_2 dissociation mechanism. Detailed studies of I_2 , when properly corrected for spin-orbit relativistic effects, indicate that there are no electronically excited states which lie low enough for excitation transfer in a single collision with $O_2[{}^1\Delta_g]$. Studies of electronic-vibrational excitation transfer indicate a small cross-section for the reaction: $O_2[{}^1\Delta_g] + I_2[X {}^1\Sigma_g^+] \rightarrow O_2[{}^3\Sigma_g^-] + I_2^+$ ($V=40$). Thus, an alternate species in the iodine system is indicated in the dissociation mechanism. Our studies indicate that I_3 is the most probable reservoir species in the dissociation mechanism. This molecule is chemically stable relative to $I + I_2$ and exhibits a manifold of excited electronic states that are accessible via $O_2[{}^1\Delta_g]$ excitation. A review of the spectroscopic evidence for I_3 has been carried out and an analysis of the nature of the low-lying electronic states of I_3 has been performed.

*To be published in the Chemical Physics Letters. Supported in part by the Air Force Office of Scientific Research under Contract F49620-81-C-0097.

APPENDIX D

REACTION OF GROUND AND EXCITED STATE
YTTRIUM ATOMS WITH OXYGEN*

L. Lynds, B. A. Woody, H. H. Michels[‡], R. H. Hobbs
 United Technologies Research Center
 East Hartford, Connecticut 06108

ABSTRACT

The reaction of optically pumped $Y(^4F_J)$ with $O_2(X^3\Sigma_g^-)$ leads to the formation of $YO(B^2\Sigma^+)$ by $Y(^4F_J) + O_2(X^3\Sigma_g^-) \rightarrow YO(B^2\Sigma^+) + O(^3P)$. This reaction channel is energetically unavailable to the ground ($^2D_{3/2}$) state of Y which only reaches the $YO(A^2\Pi)$ manifold. A double resonance technique was used to generate the $Y(^4F_J)$ states through radiative cascading and, simultaneously, as a probe for concentrations by direct absorption measurements. Exponential decay of Y in response to oxygen pressure suggests a pseudo first order kinetic mechanism. A comparison of the relative reactive cross sections indicates that the metastable $Y(^4F_J)$ states are more reactive than the $Y(^2D_{3/2})$ ground state. Despite the small separation between the spin-orbit states (200 cm^{-1}), significant differences in reactivity were observed. Cross section ratios comparing the quartet states 4F_J to the ground state $^2D_{3/2}$ are:

$$\sigma(^4F_{7/2})/\sigma(^2D_{3/2}) \approx 1.6 \text{ and } \sigma(^4F_{5/2})/\sigma(^2D_{3/2}) \approx 10.$$

Details of the experiments will be discussed and a theoretical interpretation based on spin-orbit correlations between reactant and product states will be presented.

*To be published in Chemical Physics Letters, 1983.

[‡]Supported in part by Air Force Office of Scientific Research Contract F49620-81-C-0097.

APPENDIX E

ENERGETICS AND MECHANISM OF $\text{Mg}[^3\text{P}]$ PRODUCTION
IN $\text{Mg}/\text{N}_2\text{O}/\text{CO}$ FLAMES*

H. H. Michels[†] and R. A. Meinzer
United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

The $\text{Mg}/\text{MgO}/\text{CO}$ chain reaction for the production of $\text{Mg}[^3\text{P}]$ atoms has been examined experimentally, using a purely thermal source of $\text{Mg}[^1\text{S}]$ atoms, and theoretically in terms of the potential energy surfaces for this reaction. The observed chemiluminescent emission arises from reactions involving the formation of a charge transfer $\text{Mg}^+ - \text{N}_2\text{O}^-$ intermediate. $\text{Mg}[^3\text{P}]$ atoms are formed upon reduction by CO of the lowest triplet component of this charge transfer complex.

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APPENDIX F

ENERGETICS OF IF FORMATION*

H. H. Michels[†]United Technologies Research Center
East Hartford, Connecticut 06108

ABSTRACT

The $B \ ^3\Pi_{0+} \rightarrow X \ ^1\Sigma_{0+}$ electronic transition in IF appears to be a very attractive candidate as a short wavelength chemical laser system. In order to evaluate whether a chemical pumping scheme can be devised to populate the $B \ ^3\Pi_{0+}$ state, detailed studies of the low-lying electronic structure of IF have been undertaken. These studies were carried out using an ab initio approach based on a (λ, S) coupling scheme. Spin-orbit effects were evaluated using a one-center perturbative treatment.

Our results indicate that the $B \ ^3\Pi_{0+}$ state is predissociated by both the $c \ ^3\Pi_{0+}$ and $Y \ ^3\Sigma_{0+}^-$ states; the lowest predissociation is by $c \ ^3\Pi_{0+}$ at the $v'=10$ level of the B state. The lowest reservoir state, $A' \ ^3\Pi_2$, lies at approximately $13,600 \text{ cm}^{-1}$, thereby ruling out direct excitation processes for IF with pump molecules such as O_2 [$a \ ^1\Delta_g$].

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